

AD-A210 573

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## REPORT DOCUMENTATION PAGE

2a. SECURITY CLASSIFICATION AUTHORITY DTIC ELECTE III 27 1989		1b. RESTRICTIVE MARKINGS None	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release. Distribution unlimited.	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TECHNICAL REPORT #6		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Massachusetts	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Lederle Graduate Research Tower Amherst, MA 01003		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington VA 22217-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington VA 22217-5000		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. N00014-87 PROJECT NO. k-0464 TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) COMPUTATIONAL MODELING OF PI-CONJUGATED POLYRADICALS unclassified			
12. PERSONAL AUTHOR(S) Paul M. Lahti, Andrew S. Ichimura			
13a. TYPE OF REPORT Preprint	13b. TIME COVERED FROM 9-30-88 TO 5-30-89	14. DATE OF REPORT (Year, Month, Day) 1989 May 30	15. PAGE COUNT 13
16. SUPPLEMENTARY NOTATION Submitted for publication in Molecular Crystals, Liquid Crystals.			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Organic radicals and polyradicals, organic magnetic materials High-spin organic molecules, molecular orbital theory.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Spin-spin coupling in a number of aryloxy-based polyradicals is computationally investigated using the AM1 semiempirical molecular method with configuration interaction. The qualitative accuracy of ground spin state prediction by parity based models is confirmed by computational predictions, and experimental results to date for a variety of model diradical systems is in accord with computationally predicted ground state multiplicities. The method is of general utility in identifying polyradical systems of potential interest for synthesis a possible organic high-spin magnetic materials.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Non-classified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth Wynne, Acting Director, Chemistry		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH  
Contract # N00014-87-K-0464  
R&T Code 413c037  
Technical Report #6

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
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A-1	

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by

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Prepared for

Publication in

Molecular Crystals, Liquid Crystals

(A Special Edition for the Symposium on Ferromagnetic and  
High Spin Molecular Based Materials at the 197th American  
Chemical Society Meeting)

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Submitted 19 May, 1988

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## COMPUTATIONAL MODELING OF PI-CONJUGATED POLYRADICALS

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**Abstract** Spin-spin coupling in a number of aryloxy-based polyradicals is computationally investigated using the AM1 semiempirical molecular orbital method with configuration interaction.

### INTRODUCTION

Recent interest in synthesizing organic molecules with very high spin ground states has been spurred by the hope that a variety of such materials could in principle have superparamagnetic or ferromagnetic properties of potential use as magnetic information storage systems. Several groups have reported work on charge-transfer based ferromagnetic materials<sup>1-3</sup> or organic polymeric materials<sup>4-5</sup> with some ferromagnetic domains present. Organic polyradical macromolecules<sup>6-7</sup> are one general type of material with potentially interesting magnetic properties. A substantial body of experimental work has been published concerning the generation of several oligomeric polycarbenes<sup>7</sup> under cryogenic solid state conditions, which in summary confirms the idea that linkage of unpaired electrons through conjugated pi-systems can indeed lead to overall very high-spin materials.

Our group has been interested in synthesis of pi-conjugated polyradical model systems based upon coupling of phenoxyl radicals by a variety of connecting spacer groups, such as heteroatoms and olefinic spacer groups -X- in the general model Phenoxyl-X-Phenoxyl. In order to select in a reasonably rational manner the model systems most likely to lead to high spin ground state (GS) molecules, we have refined a computational algorithm similar to others used by us<sup>8</sup> in previous GS multiplicity

computations for non-Kekulé molecules. The algorithm to be described has been tested for agreement with experimentally observed GS multiplicities for a variety of known diradical systems,<sup>8</sup> and has proven effective by this criterion. We therefore have adapted the diradical algorithm for use with higher polyradicals, with the results described below.

### COMPUTATIONAL METHODS

We have used the AM1 hamiltonian<sup>9</sup> in AMPAC<sup>10</sup> to obtain optimized geometries for all non-Kekulé molecules described in this work. Geometries were obtained using restricted Hartree-Fock wavefunctions (RHF) at the multiplicity of the resonance structure of highest Kekulé bondedness for a given structure. Use of triplet state unrestricted Hartree-Fock (UHF) rather than RHF wavefunctions for diradicals made only small geometric differences which we feel are not crucial to the qualitative conclusions we will draw, despite excellent arguments which have been advanced for the use of UHF geometries<sup>11</sup> in polyradical optimizations. In general, optimizations were carried out *with planar constraints*. Although assumption of a planar geometry is as likely as not to prove specious under solution conditions, some planarization of a largely aromatic oligomer under solid state conditions seems reasonable. Since these computational studies are meant at this stage to investigate the qualitative nature and approximate magnitude of spin-spin coupling in a variety of experimentally reasonable polyradical systems with different connectivity and functionality, we feel that the planar constraint is a useful simplification. We must keep in mind in the following discussions the caution that extreme torsion and deconjugation of radical containing units or of  $\pi$ -conjugating spacers connecting them might be expected to truncate the effects of radical-radical coupling.<sup>12</sup>

Upon obtaining the appropriate geometries, configuration interaction (CI) computations using AM1 were carried out on the systems of interest. Generally, an

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active space consisting of the highest three occupied and highest four unoccupied and partially occupied MO's (if one considers the configuration with the maximum electron pairing) was used for CI, with the state of highest multiplicity in a resonance structure of highest Kekulé bondedness used as the reference configuration. The lowest energy states in each spin manifold were compared to assess semi-quantitatively the GS multiplicity and the energetic gap to the next state.

### RESULTS

Figure 1 shows the generic structures 1-3 by which we studied GS multiplicity as a function of oligomer size for  $n = 1-5$ . All molecular geometries up to the trimers were computed with planar constraints as described above, and were assumed to have all oxy radical centers in the *syn* conformation.<sup>13</sup> For 2-3 ( $n=4-5$ ), the monomeric repeat unit was simply taken geometrically as being the same as the central unit in the trimer (with only *s-trans* geometry double bonds used) to avoid the size of a complete optimization of the tetramer. This is not an unreasonable approximation, since a repeat unit is readily identifiable upon examination of the optimized trimeric geometry. Table 1 shows the AM1-CI results for the seven orbital with six electron (7MO/6e) CI active space for 1-3 ( $n=1-5$ ).

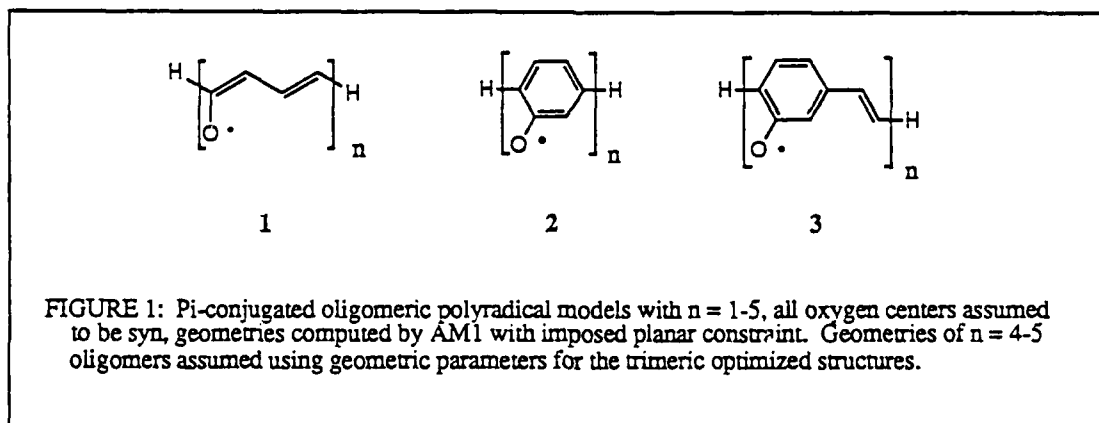
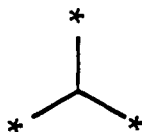


TABLE 1: Energy Gaps Between Ground and Excited States of Oligomers 1-3.

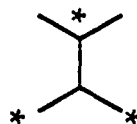
Structure	Oligomer Length	$S_{GS}^b$	$DE_{GS-ES}^c$
1	2	1	3.3
	3	3/2	0.5
	4	2	0.3
	5	5/2	0.3
2	2	1	7.3
	3	3/2	4.7
	4	2	4.3
	5	5/2	3.9
3	2	1	3.5
	3	3/2	2.7
	4	2	2.7
	5	5/2	2.2

<sup>a</sup>See Figure 1 for qualitative structures. <sup>b</sup>Ground state (GS) spin quantum number (singlet=0, triplet=1, etc.). <sup>c</sup>Energy gap in kcal/mol between GS and next higher excited state (ES) of spin  $S_{EX} = S_{GS} - 1$ . For  $DE > 0$ , the GS is high spin.

Most notable in the results of Table 1 is that a computed high spin GS is in all cases favored where expected by qualitative connectivity or parity based theories. Such theories are fully described in the literature,<sup>14-18</sup> and will not be expanded upon here, except to briefly describe the Ovchinnikov parity-based model,<sup>14</sup> which we have found quite useful. This model predicts that for any alternant, fully-conjugated pi-system with  $N^*$  alpha-spin centers and  $N^0$  beta-spin centers, the ground state (GS) spin multiplicity  $S = (N^* - N^0)/2$  would be preferred ( $S$  = spin quantum number).



$N^* - N^0 = 3 - 1$   
triplet GS



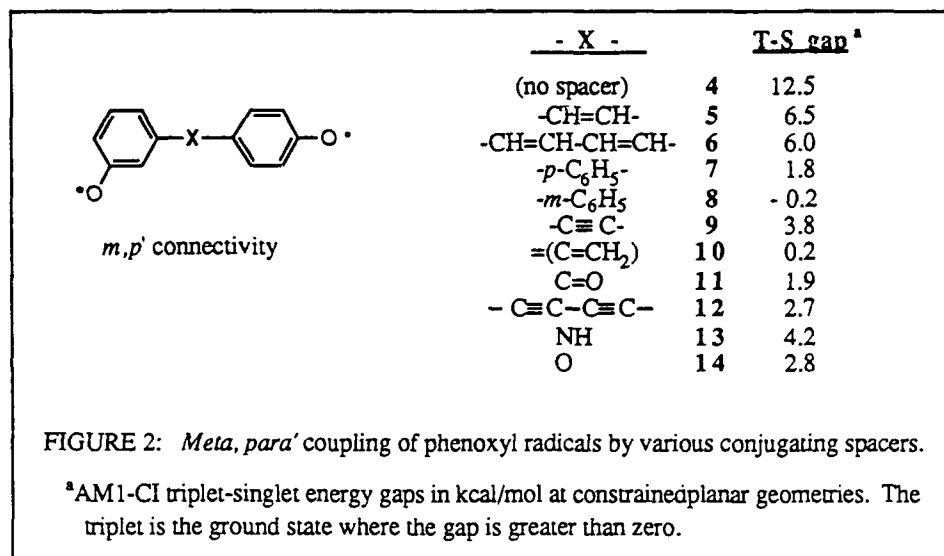
$N^* - N^0 = 4 - 1$   
singlet GS

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The magnitude of this preference is smallest for **1** at  $< 1$  kcal/mol for the  $n = 3-5$  cases. This may reflect the similarities between **1** and substituted oxyallyl systems, for which *ab initio* results by ourselves<sup>19</sup> and others<sup>20</sup> suggest a small or negative T-S gap. For species **2-3**, modest GS-ES gaps are found. We feel that these results imply that the high density of pi-orbitals available in a polymeric system involving phenoxyl radicals (rather than a simpler pi-system) may be conducive to allowing an extra stability of the high spin GS relative to the lower spin excited state (ES). In addition, for the phenoxy-based systems, the magnitude of the gap at this level of theory suggests that there will be some energetic separation of manifolds of different multiplicity in oligomers of modest length, rather than mixtures of several states of different multiplicity into closely spaced energy "bands". Naturally, it would be unreasonable to overinterpret the absolute numbers obtained by our algorithm, but we feel that the qualitative trend of these numbers clearly implies that phenoxy-based conjugated oligomers of the connectivity shown in **2-3** (or polymers with a similar number of conjugated polyradical units) should be favorable for production of high spin GS molecules.

Figure 2 shows the results of AM1-CI 7MO/6e computations for two phenoxy systems linked in a *meta,para'* fashion by a variety of connecting units in diradical models **4-14**. For systems **4-6** where no spacer, a 1,2-ethenediyl spacer, and an *s-trans* 1,4-butadienediyl spacer are used respectively, the triplet-singlet (T-S) energy gap remains fairly large, implying that such through-conjugating ethylenic units intrinsically allow good spin communication between the radical sites. Similarly, the acetylenic and diacetylenic spacers in models **9** and **12**, while quantitatively not as effective as the ethylenic spacers, are qualitatively still predicted to be effective. The modest gap for the *para*-phenylene spacer (2.3 kcal/mol) implies that the phenyl spacer, while allowing spin communication, is not as effective as the ethylenic and acetylenic spacers. Connectivity is important in these systems, since the 1,1-

ethenediyl and *meta*-phenylene spacers result in reduction or reversal of the preference of the high spin GS in models **8** and **10**, as would normally be



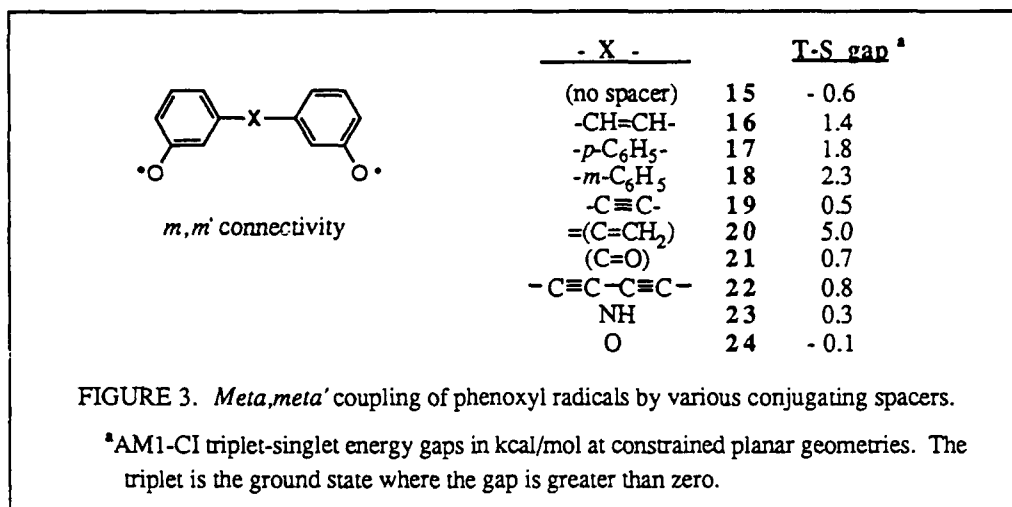
expected by the application of the the Ovchinnikov criterion in such systems. Overall, therefore, a variety of pi-connectors are predicted to have utility in allowing spin communication to produce high spin GS's in these model computations for *meta,para'* coupling, all of which are experimentally feasible and under investigation within our group.

Figure 3 shows T-S gaps for diradical models **15-24**, which have *meta,meta'* linking of phenoxy centers rather than *meta,para'*. Comparison of these data to those of Figure 2 shows that the *m,m'* isomers with  $N^* = N^0$  and where -X- is a through-conjugating spacer all have substantially reduced or negative T-S gaps relative to the *m,p'* isomers with  $N^* > N^0$ . This semiquantitative finding is qualitatively consistent with the parity based criteria, and further reinforce the importance of connectivity in GS spin prediction. We do not predict a singlet GS for **15**, **16**, **18**, or **20**, but the small T-S gaps in these cases where  $N^* = N^0$  do indicate that the Ovchinnikov parity based model is indeed obeyed in a less rigorous fashion, through a decrease in



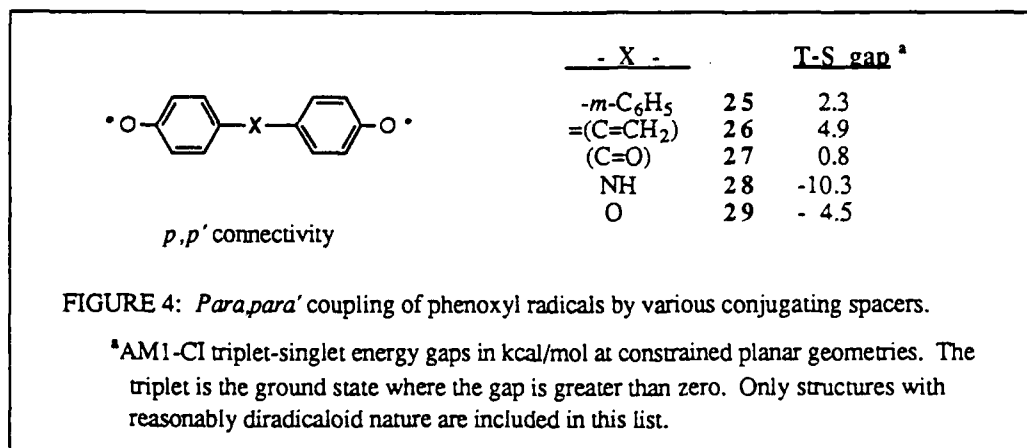
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spin communication between the radical centers, and commensurately lower T-S gaps relative to the cases where  $N^* > N^0$ . This is also shown by the larger gaps in the two



hydrocarbon-coupled systems where  $N^* > N^0$ , **17** and **20**; thus the small gaps in most of the systems **15-24** are due to spin-spin coupling effects, and not merely to the *meta,meta'* substitution pattern.

Figure 4 shows AM1-CI 7MO/6e results for the T-S gaps of *para,para'* linked models **25-29**. For many spacers -X- a closed-shell Kekulé structure is energetically best with *para,para'* coupling. We did not investigate such species, but only those that are non-Kekulé molecules or at least diradicaloids. Again, our results for pi-



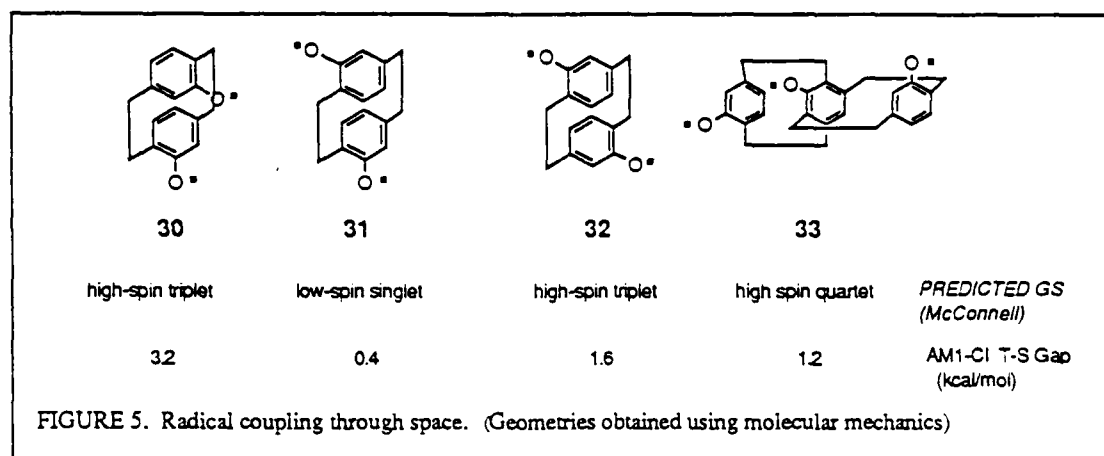
conjugating spacers shows that the Ovchinnikov parity criterion is obeyed, with much larger T-S gaps for systems that have  $N^* = N^0 + 2$ , as expected.

Overall, we can classify the T-S energy gap results as a function of different spacers for Figures 2-4 into three categories. First, there are the through-conjugating spacers (e.g. 1,2-ethenediyl and *para*-phenylene). In these the Ovchinnikov parity model is roughly obeyed, with much stronger T-S splitting in systems where  $N^* > N^0$  compared to those where  $N^* = N^0$ . Second, there are cross-conjugated pi-spacers, exemplified by 1,1-ethenediyl, carbonyl, and *meta*-phenylene. For the 1,1-ethenediyl and *meta*-phenylene spacers, the Ovchinnikov criterion is followed with a reasonably strong T-S splitting. It is worth noting that the variety of substitution patterns yielding a non-Kekulé structure for cross-conjugated spacers is larger for than for through-conjugated spacers (the *para,para'* connectivity for through-conjugation usually yields Kekulé structures). The results predicted for the cross-conjugating carbonyl spacer are not as clear as those for the hydrocarbon cross-conjugated spacers, possibly due to the effects of frontier orbital splitting by the oxygen in the carbonyl, and due to the especially stable nature of the carbonyl unit. The desire of a carbonyl unit to remain isolated and to avoid efficient radical coupling in the oxyallyl system  $[\text{CH}_2-(\text{C}=\text{O})-\text{CH}_2]$  has been implicated in the small T-S energy in oxyallyl<sup>19-20</sup>; similar considerations may render the coupling in **11**, **21**, and **27** weak regardless of connectivity parity, as our computations imply. Thus, as attractive as a carbonyl spacer may be synthetically, it may constitute a less effective choice of a cross-conjugating spacer than 1,1-ethenediyl for linking radicals.

Thirdly, we may note that two-electron heteroatom spacers NH and O act quite differently from the other pi-spacers. It was been noted that such two-electron/one center (2e/1c) spacers may be expected to act as antiferromagnetic coupling units by a superexchange mechanism for benzylic and phenylcarbenic systems.<sup>21</sup> We note the same qualitative antiferromagnetic coupling for connection of phenoxyl radicals.

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For instance, despite being non-Kekulé, the *meta,meta'* systems **23** and **24** have nearly isoenergetic triplet and singlet states. The *para,para'* connected species **28** and **29** may be considered to be very strongly coupled to give favorable singlet states; however, this is somewhat misleading since reasonable zwitterionic Kekulé resonance structures may be formulated for the *para,para'* connectivity with  $-X- = NH, O$ , and so these should probably not be considered in the same sense as the obviously non-Kekulé isomers. Additional evidence for this is provided by the fact that the CI wavefunctions of **28** and **29** show diradicaloid rather than diradical character.<sup>8b</sup> However the state ordering in the non-Kekulé *meta,meta'* and *meta,para'* coupled cases is entirely consistent with antiferromagnetic coupling by the  $2e/1c$  spacers.



Finally, Figure 5 shows AM1-CI 7MO/6e results for the T-S gaps of two phenoxy systems constrained to pseudo *ortho*, *meta*, and *para* through-space interactions in a *para*-cyclophane system. McConnell<sup>22</sup> has qualitatively predicted high spin GS's in systems where the product of sites of overlapping spin density is negative. Iwamura has experimentally confirmed this by synthesis of *bis*(phenyl carbene) systems linked through the *para*-cyclophane skeleton.<sup>23</sup> Our results of Figure 5 show triplet GS's for **30** and **32**, but with a very small T-S gap for the pseudo-*meta* isomer **31**. This constitutes a qualitative computational confirmation of the McConnell model for coupling of phenoxy radicals, similar to a theoretical result

shown recently for benzylic radicals.<sup>24</sup> The experimental results by Iwamura *et al.*<sup>23</sup> for coupled carbenes are also in accord with the McConnell relationship. For the three-ring stacked system **33**, we find a high-spin quartet GS as predicted by the McConnell model. Such systems are important as models for three dimensional stacking between radicals in a crystal, and for solid state interactions between units of interacting polymer chains in the solid state. We are also working on synthesis of these model diradicals, and will report in due course the progress in this area.

### SUMMARY AND CONCLUSIONS

In summary, we have found that the AM1 molecular orbital method with limited CI allows for a useful realistic conceptual treatment of connectivity and functionality effects in large pi-conjugated polyradicals which are too large to be practically investigated by ab initio techniques. The method has proven qualitatively correct by comparison to experimental ground state spin multiplicity determinations for several known diradicals, and is therefore worth extending to the still-unknown oligomeric polyradical models examined in this paper. Assuming that the method is qualitatively correct, we may draw the following general conclusions from the set of data in this work:

1. Planar pi-conjugated polyoxyradicals favor high spin GS's for higher oligomers, as predicted by qualitative theory.
2. A variety of conjugating pi-spacers allows reasonably efficient coupling of phenoxyl radicals to give high spin triplet GS's in model diradical computations. Through-conjugating and cross-conjugating spacers are ferromagnetic coupling spacers and give results in general accordance with parity based GS spin state predictive models. Two electron/one center heteroatom spacers such as NH and O act as antiferromagnetic spacers.

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3. Connectivity effects in different diradicals are in rough accord with parity based models, except that we often find high spin states qualitatively somewhat favored even where low spin states are predicted by such models. We feel that the parity rules are more safely interpreted to predict when a high spin state is greatly ( $N^{\bullet} > N^0$ ) favored over a low spin state, or whether the two will be quite similar in energy ( $N^{\bullet} = N^0$ ).

4. Three-dimensional stacking of phenoxyl radicals appears to follow the McConnell model based upon the favoring of overlap between sites of opposite spin density. The magnitude of coupling through space is, however, fairly modest and may make design of truly three-dimensional organic ferromagnets difficult.

While much experimental and computational work remains to be done on the types of polyradical models discussed in the paper, we feel that the kind of semiquantitative results obtainable by our procedure proves the usefulness of semiempirical MO-CI theory in probing the spin multiplicity and other electronic properties of polyradicals. Use of such methods for rational selection of key model systems for experimental synthesis is by our method easy, cheap, and useful for conceptual analysis of various electronic properties.

### ACKNOWLEDGEMENTS

We acknowledge the support of the Office of Naval Research and the National Science Foundation (CHE-8712319) for this work. A University of Massachusetts Faculty Research Grant was also given in support of the computational facilities used in this work. Supplementary material includes AMPAC files describing input geometries for systems described in this work, and are available from PML upon request at the address indicated on the title page. Support from the University of Massachusetts for computational facilities at the chemistry department is gratefully acknowledged.

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12. We find that for a number of randomly selected model systems, fully relaxed AM1 geometry optimization leads to modest amounts of torsion and deconjugation, but with only minor quantitative decreases in T-S gaps. Roughly speaking, torsions up to at least 20° in most systems studied in this paper do not change qualitative conclusions. A more detailed description of computations at unconstrained geometries, and of the effects of torsion upon spin-spin coupling in systems such as those described in this paper will be published at a future time.
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